# Polytopic Ligand Systems: Synthesis and Complexation Properties of a 'Crowned' Phthalocyaninet

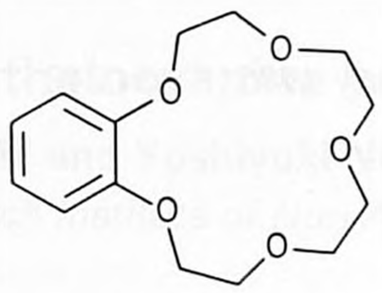
**Ron Hendriks, Ot E. Sielcken, Wiendelt Drenth, and Roeland J. M. Nolte***

*Department of Organic Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands*

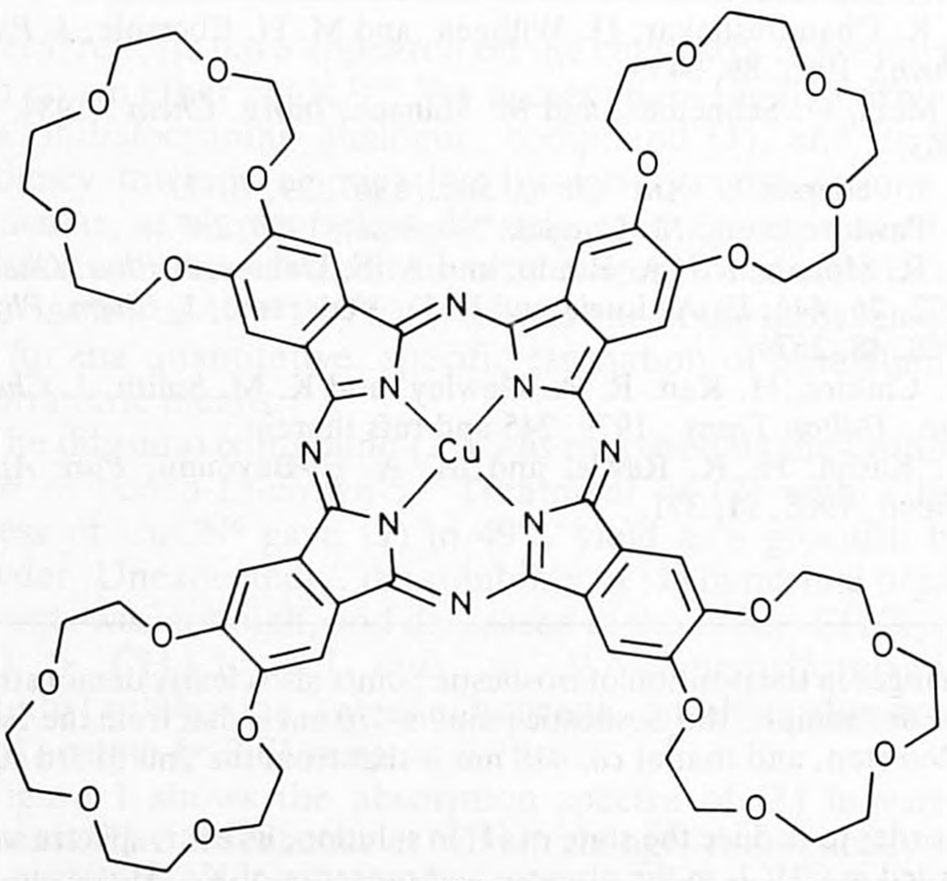
The synthesis is described of a phthalocyanine that contains four 15-crown-5 rings; $K^+$ ions induce dimerization of the phthalocyanine, whereas $Li^+$ and $Bu^tNH_3^+$ ions do not.

We designed the polytopic ligand (**2**) as part of a programme aimed at the development of multifunctional catalysts and carrier systems from easily accessible host molecules. Compound (**2**) contains a metal centre that is complexed by a phthalocyanine ring and four crown ether binding sites. Its synthesis and binding properties are described.

Benzo-15-crown-5 (**1**)[1] was brominated ($Fe–Br_2$, solvent $CH_2Cl_2$) to give 4,5-dibromobenzo-15-crown-5 in 65% yield. The latter compound (1.0 mmol) was refluxed for 20 h with CuCN (5 mmol) in *N,N*-dimethylformamide (1.5 $dm^3$). A small amount of pyridine (0.1 $dm^3$) was added as a catalyst. After work-up (aqueous ammonia, extraction with chloroform) the solid residue was subjected to column chromatography (neutral alumina, eluant $CHCl_3$–MeOH, 10 : 1 v/v). Compound (**2**) was obtained as a green, almost black powder in 35% yield (m.p. > 200 °C).‡



(**1**)



(**2**)

The complexation properties of compound (**2**) were evaluated by u.v.–visible spectroscopy. The free host shows a spectrum which is characteristic for a monomeric copper phthalocyanine.[2] On addition of KBr this spectrum changes and a new spectrum, attributable to dimeric phthalocyanine appears (Figure 1, inset). On increasing the concentration of

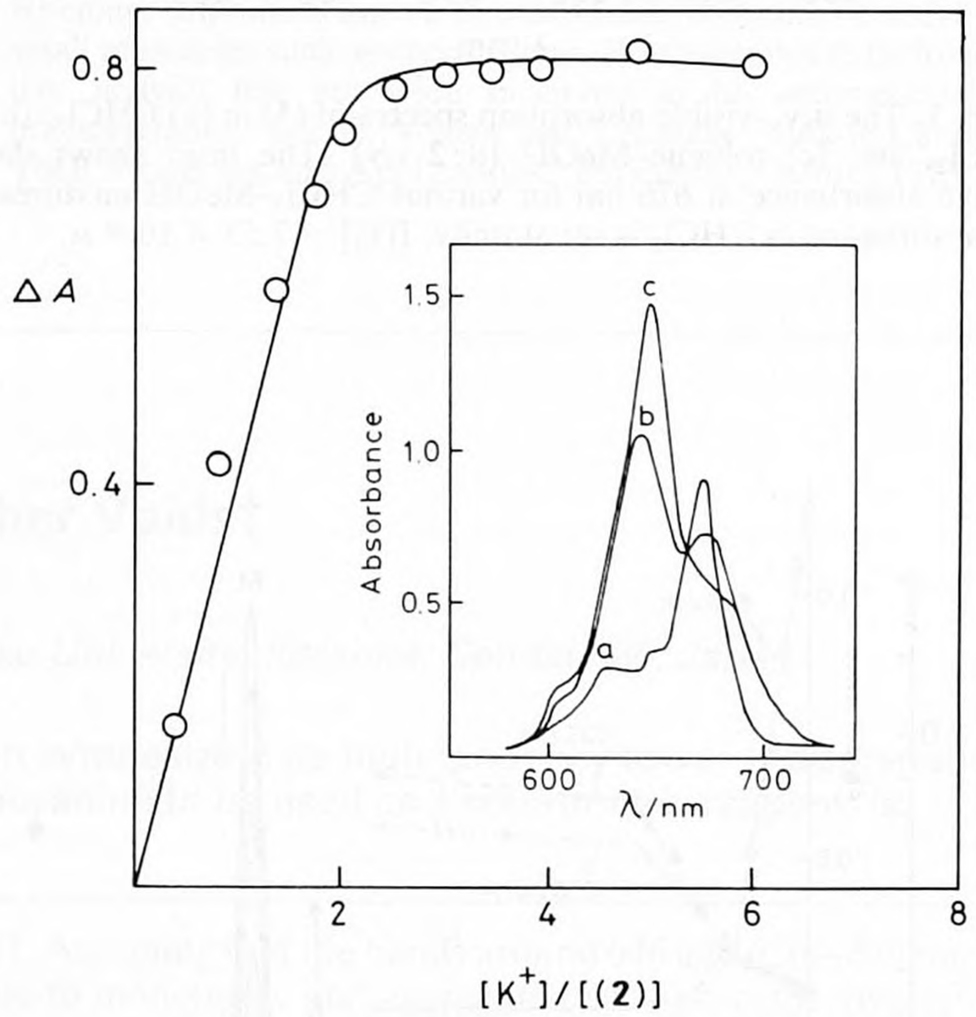



**Figure 1.** Absorbance increase, $\Delta A$, *vs.* ratio of cation to crown–phthalocyanine. Inset: visible absorption spectra of (a) host (**2**) in chloroform ($10^{-5}$ mol $dm^{-3}$), (b) (**2**) +1.5 equiv. of KBr and (c) (**2**) +6 equiv. of KBr.

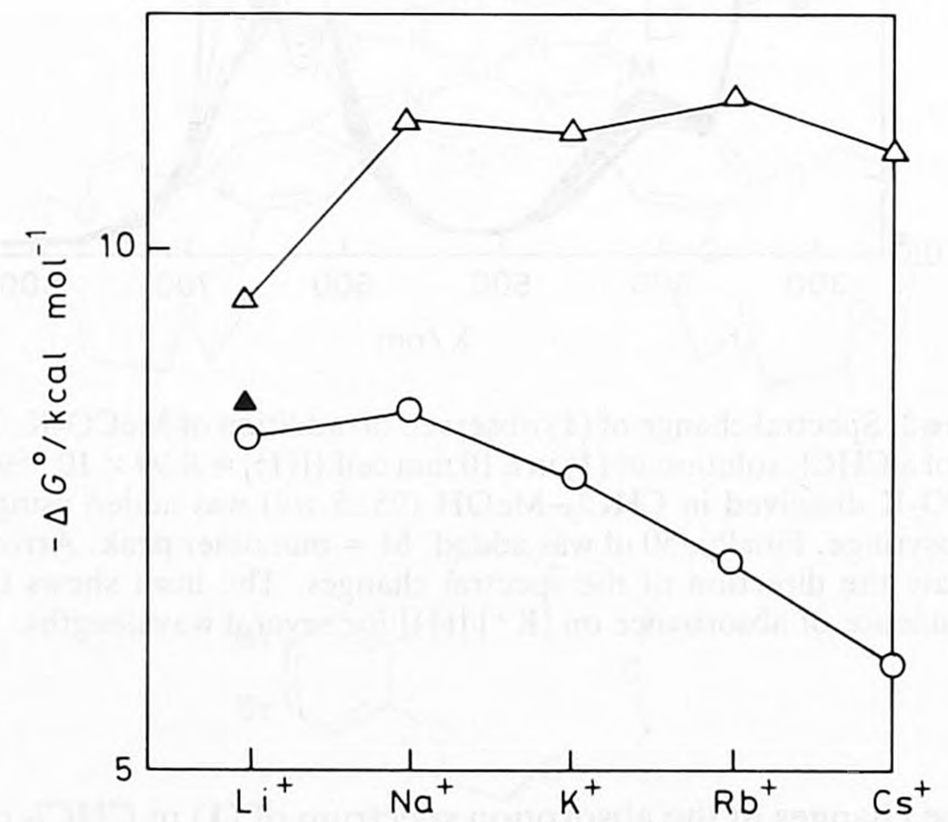



**Figure 2.** Free energies of binding of picrate salt guests to host (**1**) (1 : 1 complex, (○) and to host (**2**) (2 : 1 complex: △; 1 : 1 complex ▲).

† Since the submission of this communication, related work was published by A. R. Koray, V. Ahsen, and O. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932. The preceding communication submitted independently, also reports related work.

‡ Compound (**2**) gave analytical and spectroscopic data consistent with its structure.

KBr the spectrum of monomeric phthalocyanine gradually disappears. A plot of the increase in absorption at 630 nm as a function of the amount of added KBr (Figure 1) shows an inflection point at a $K^+$ to phthalocyanine ratio of *ca.* 2:1. This indicates that the crown ether rings of (**2**) and $K^+$ ions form complexes of stoicheiometry 8:4 (host:guest). Adding $Li^+$ and t-butylammonium ions to (**2**) did not change the u.v.–visible spectrum of this compound. From this we assume that these ions form 4:4 complexes with (**2**).

The free energies of complexation ($-\Delta G^\circ$) for a number of cations by host molecules (**1**) and (**2**) were determined by the picrate extraction method.[3] Figure 2 compares the apparent $-\Delta G^\circ$ values (kcal mol$^{-1}$§) for $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ picrate complexes of (**2**), assuming 2:1 complexation, with those of (**1**), which forms 1:1 complexes.¶ The latter compound displays the normal binding profile for this type of host, *i.e.* the $-\Delta G^\circ$ values become smaller when the diameter of the guest molecule increases. Compound (**2**), however, shows a different behaviour. It has a high affinity for $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ ions, with little or no structural recognition within the series, but a relatively low affinity for $Li^+$ ions. This binding profile supports the idea that large ions induce dimerization of the phthalocyanine rings.

A number of possible applications can be envisaged for molecule (**2**), for instance in the field of catalysis (*e.g.* binding of substrate molecules to the crown ether rings and reaction with ligands co-ordinated to the metal centre) and in the field of ion transport. Regarding the latter application, it is of interest that metal phthalocyanines (Pc) with suitable ligands L (–O–, $CN^-$, pyrazine) will readily form cascade complexes of the type $[Pc–L–Pc–L]_n$.[4] For (**2**) this will lead to stacking of the crown ether rings and the formation of extended channels. Such channels can bind and transport ions as we have shown previously.[5] Work along these lines is in progress and details will be published in a full paper.

*Received, 30th May 1986; Com. 724*

## References

1 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
2 F. H. Moser and A. L. Thomas, 'The Phthalocyanines,' CRC Press, Boca Raton, 1983, vol. 1, p. 61.
3 R. J. M. Nolte and D. J. Cram, *J. Am. Chem. Soc.*, 1984, **106**, 1416.
4 B. N. Diel, T. Inabe, N. K. Jaggi, J. W. Lyding, O. Schneider, M. Hanack, C. R. Kannewurf, T. J. Marks, and L. H. Schwartz, *J. Am. Chem. Soc.*, 1984, **106**, 3207.
5 U. F. Kragten, M. F. M. Roks, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1985, 1275.

§ 1 cal = 4.184 J.

¶ Compound (**1**) [$K \times 10^{-5}$/(dm$^3$ mol$^{-1}$), $-\Delta G^\circ$/kcal mol$^{-1}$ for 1:1 complex]: $Li^+$, 11, 8.2; $Na^+$, 14.5, 8.4; $K^+$, 6.5, 7.9; $Rb^+$, 1.4, 7.0; $Cs^+$, 0.3, 6.1; $Li^+$–(**2**) complex: 25, 8.7; compound (**2**) [$K \times 10^{-7}$/(dm$^3$ mol$^{-1}$)$^2$, $-\Delta G^\circ$/kcal mol$^{-1}$ for 2:1 complex]; $Li^+$, 1.1, 9.6; $Na^+$, 18, 11.3; $K^+$, 16, 11.2; $Rb^+$ 23, 11.4; $Cs^+$ 9.0, 11.0.

# Regiospecific Synthesis of Terminal, Oxyfunctionalized Methyl Ketone Enamines *via* Catalytic Aminomercuriation of Prop-2-ynyl Esters and Ethers

**José Barluenga,* Fernando Aznar, Ramón Liz, and Carmen Postigo**

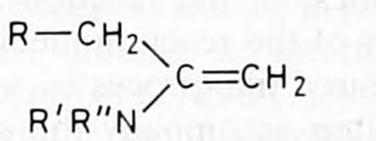
*Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain*

Catalytic aminomercuriation of 1-substituted prop-2-ynyl esters and ethers (**5**) provides a mild, simple, and regiospecific route to the terminal functionalized enamines (**6**) despite the fact that they are potentially isomerisable to their internal form; hydrolysis of (**6**) furnishes α-oxyketones (**7**).

Enamines[1] derived from alkyl methyl ketones, obtained by a variety of methods, have usually been reported to exist as a mixture of isomers differing in the terminal (**1**) or internal (**2**) double bond position.[2] In fact, apart from a series of enol ether- and enol sulphide-enamines, (**3**) and (**4**), recently prepared by us *via* catalytic aminomercuriation of prop-2-ynyl ethers and sulphides,[3] only some isolated instances are known in which the location of the double bond is unambiguous [*e.g.*, (**1a**),[2c] (**2a**)[4]]. Since both electronic and steric factors[2f,5] seem to influence the regioisomer distribution, we decided to employ the more hindered 1-substituted prop-2-ynyl esters and ethers (**5**) as unsaturated substrates in catalytic aminomercuriation processes.[6]

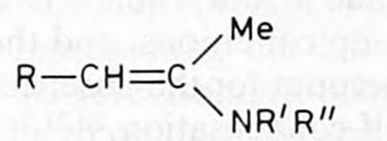
When a 1-substituted prop-2-ynyl ester or ether (**5**) was treated with an excess of piperidine or morpholine, in the presence of mercury(II) acetate as catalyst, the corresponding β′-oxysubstituted enamine (**6**) was regiospecifically obtained, the internal isomer not being detected in the crude reaction mixture, according to the $^1$H n.m.r. spectra (90 MHz)†

† In some instances, *ca.* 5% of the corresponding acetamide was observed as by-product.



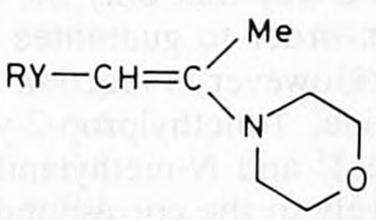
(**1**)

**a** R = Pr$^i$, R′ = R″ = Me

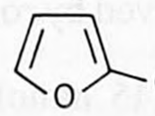


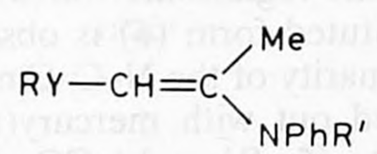
(**2**)

**a** R = Ph, R′R″ = $(CH_2)_2O(CH_2)_2$



(**3**)

RY = $CH_2$=CH–$CH_2O$,  , PhO, PhS



(**4**)

RY = MeO, $CH_2$=CH–$CH_2O$, $PhCH_2O$, PhO, PhS; R′ = Me, Et